(19) Eur päisches Patentamt
European Patent Office
Offic européen des br vets

(11) Publication number: **0 599 251 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 93118776.9

(22) Date of filing: 22.11.93

(51) Int. Cl.⁵: C10M 169/04, C10M 171/00, //C10N30/08,C10N40/00, (C10M169/04,107:50,129:10, 129:54,125:06,131:12,135:04, 135:06,135:10,135:18,135:22, 137:02,137:04,137:08,137:10, 159:12)

(30) Priority: 20.11.92 JP 312190/92

(43) Date of publication of application: 01.06.94 Bulletin 94/22

(84) Designated Contracting States: DE GB IT

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(54) **Fluid composition for use in viscous coupling.**

(57) The present invention provides a stable working fluid for use in a viscous coupling which is insusceptible to viscosity decreases due to thermal decomposition as well as viscosity increases or gelation, which comprises a specific polyorganosiloxane as a base oil having one or more selected from the group consisting of sulfonate, phenate and salicylate incorporated therein, and which may further comprises sulfur, phosphorus and chlorine compounds incorporated therein.

EP 0 599 251 A1

FIELD OF THE INVENTION

The present invention relates to a fluid composition for use in a viscous coupling insusceptible to viscosity decreases and gelation during prolonged use.

BACKGROUND OF THE INVENTION

A viscous coupling is a shaft coupling which depends on the viscosity of a working fluid for its action and is mounted in a differential mechanism or on a propeller shaft as an aid to achieving cruising stability of automobiles or extricating the automobile from off-road conditions. Its durability largely depends on the performance of the working fluid with which it is filled. A viscous coupling is composed of a housing, a hub and several tens of thin annular iron plates attached to each of the housing and the hub, with a highly viscous working fluid being confined in the coupling. When a difference in rotational speed is created between the plate assemblies on the hub and housing sides, a shear force is exerted on the two plate assemblies and the torque generated on account of the viscosity of the working fluid is either transmitted or used to control the difference in rotational speed. The construction of a typical viscous coupling is described in JP-B-58-48779 (The term "JP-B" as used herein means an "examined Japanese patent publication").

As described above, a viscous coupling depends on the viscous drag of the working fluid for its action and if it is to be installed in an automobile, it is required that the coupling be of the smallest possible size and yet be capable of generating the necessary torque. Therefore, working fluids of comparatively high viscosity have been employed with viscous couplings. Other requirements for working fluids used in viscous couplings are a small temperature dependency of the viscosity and a high stability at elevated temperatures. While silicone fluids have been conventionally used as working fluids, the most common is a dimethylpolysiloxane fluid having a viscosity of 5,000 to 500,000 centistokes (cSt) at 25 °C.

However, this fluid has a potential to become very hot due to heat generation from shearing action on the fluid or the friction between plate assemblies and it often happens that during prolonged use, the fluid's viscosity increases until it eventually gels. If the working fluid in a viscous coupling undergoes a significant change in its viscosity or if it gels, the initial setting for the performance of the viscous coupling is no longer applicable. This has been the problem with conventional working fluids or viscous couplings that requires solution. On the other hand, if the working fluid in a viscous coupling is heated to relatively high temperatures, it undergoes thermal decomposition that causes viscosity decreases, making it impossible to maintain the initial setting for the performance of the viscous coupling.

In any attempt to improve the heat resistance of polyorganosiloxane, the addition of various heat stabilizers has been studied. On the other hand, for the fluids for use in a viscous coupling, the addition of sulfur compounds (as disclosed in JP-A-64-65159 (The term "JP-A" as used herein means an "unexamined published Japanese patent application")) and phosphorus compounds (as disclosed in JP-A-2-91196) has been proposed.

While the addition of such a sulfur compound or phosphorus compound is confirmed to have a great effect of inhabiting the viscosity increases or gelation due to the polymerization or crosslinking of a polyorganosiloxane, it is not effective enough to inhibit the viscosity decreases due to thermal decomposition.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a stable working fluid for use in a viscous coupling that is insusceptible to viscosity decreases due to thermal decomposition as well as viscosity increases or gelation.

The inventors made extensive studies to develop a working fluid that overcomes the foregoing difficulties and would perform stable for a prolonged period when used in a viscous coupling. As a result, the inventors found that a stable working fluid for use in a viscous coupling that is insusceptible to viscosity decreases due to thermal decomposition can be produced by incorporating a sulfonate, phenate or salicylate in a polyorganosiloxane fluid as a base oil and that a stable working fluid for use in a viscous coupling that is also insusceptible to viscosity increases or gelation can be produced by further incorporating a sulfur, phosphorus or chlorine compound in the foregoing system. The present invention has been accomplished on the basis of this finding.

The foregoing and other objects of the present invention will become more apparent from the following detailed description and examples.

The foregoing object of the present invention can be attained by a fluid composition for use in a viscous coupling comprising the following components (A) and (B):

(A) A polyorganosiloxane having a viscosity of 500 to 500,000 centistokes at 25 °C represented by the following average unit formula (1):

$$(R^1)_a SiO_{\frac{4-a}{2}}$$

wherein R^1 represents a hydrocarbon group or halogenated hydrocarbon group; and the suffix a represents a number of 1.9 to 2.1; and

(B) one or more selected from the group consisting of sulfonate, phenate and salicylate.

DETAILED DESCRIPTION OF THE INVENTION

The base oil of the fluid composition according to the present invention is a polyorganosiloxane represented by the average unit formula (1), in which R^1 represents a hydrocarbon group or halogenated hydrocarbon group. Illustrative hydrocarbon groups are C_{1-12} straight-chained or branched, saturated or unsaturated aliphatic hydrocarbon groups (e.g., alkyl, alkenyl) and C_{6-18} aromatic hydrocarbon groups. Illustrative halogenated hydrocarbon groups are the hydrocarbon groups listed above in which at least one hydrogen atom is replaced by a halogen atom (e.g., fluorine, chlorine, bromine, iodine). Desirable aliphatic hydrocarbon groups and halogenated aliphatic hydrocarbon groups are those which have 1 to 8 carbon atoms, such as methyl, ethyl, butyl, hexyl, octyl, trifluoropropyl and octenyl groups. Exemplary aromatic hydrocarbon groups include phenyl, tolyl and xylyl groups. These groups which are bound to silicon atoms may be the same or different. Polyorganosiloxane has a straight-chained skeleton with minor amounts of branched portions being optionally present. With polyorganosiloxane compounds of the formula (1), the suffix a is close to 2.0 if they are straight-chained and have high molecular weights. The suffix a is greater than 2.0 if they have low molecular weights. The suffix a is smaller than 2.0 if they contain branched moieties.

Examples of the polyorganosiloxane to be used in the present invention include polydimethylsiloxane, polydimethyl-methylphenylsiloxane, polymethylphenylsiloxane, polydimethyl-diphenylsiloxane, polymethyl-hexylsiloxane, polymethyloctylsiloxane, polymethyltrifluoropropylsiloxane, and polydimethylmethyl-trifluoropropylsiloxane. Besides these homopolymers and copolymers, mixtures thereof may be employed.

The molecular chain of the polyorganosiloxane fluid is preferably terminated with a triorganosilyl groups, such as trimethylsilyl or triethylsilyl group.

The polyorganosiloxane fluids listed above have viscosities at 25 °C in the range of from about 500 to about 500,000, preferably from about 3,000 to about 500,000, more preferably from about 4,000 to 450,000, particularly from about 5,000 to 400,000 centistokes. If their viscosity is too low, they produce such a small viscous drag that the capacity of the viscous coupling must be greatly increased. If their viscosity is too high, they produce such a high viscous drag that excessive heat generation may impair the durability of the viscous coupling. In the composition of the present invention, the polyorganosiloxane fluid is incorporated as a base oil. The base oil content assumes the major proportion of the composition, usually in the range of from about 90 to 99.99 wt%, preferably about 95 to 99.95 wt%, of the composition.

In the present invention, the base oil (A) made of the foregoing polyorganosiloxane comprises a small amount of one or more selected from the group consisting of sulfonate, phenate and salicylate incorporated therein. These components will be further described hereinafter.

Examples of the sulfonate to be used in the present invention include metallic salts of aliphatic sulfonic acid (R^{20}-SO_3H in which R^{20} is an alkyl group) and aromatic sulfonic acid (Ar-SO_3H in which Ar is an aryl group) with the Group I and II metals of the Periodic Table. Examples of these metals include alkaline metal, alkaline earth metal (e.g., sodium, potassium, calcium, magnesium, barium, and strontium).

Sulfonates which are desirable particularly in the present invention can be easily prepared by an ordinary method which comprises allowing an alkyl-aromatic hydrocarbon to undergo reaction with fuming sulfuric acid or SO_3 gas to effect sulfonation thereof, and the allowing the sulfonated compound to undergo reaction with an oxide or hydroxide of a metal of the Group I or II of the Periodic Table in the presence or absence of carbon dioxide gas. The reaction in the presence of carbon dioxide gas produces a perbasic sulfonate, while the reaction in the absence of carbon dioxide gas produces a neutral sulfonate. (Methods for the preparation of sulfonates are described, for example, in Henry D. Drew, <u>Metal-based Lubricant</u>

Compositions, Noyes Data, 1975, pages 3 to 6 and 33 to 61). The alkylaromatic hydrocarbon to be used in the preparation method is represented by the general formula $Ar(R^{21})(R^{22})$ wherein Ar represents an aryl group, R^{21} represents a hydrogen atom or C_{10-22} alkyl group and R^{22} is preferably a C_{8-22} alkyl group if R^{21} is a hydrogen atom or C_{3-10} alkyl group if R^{21} is an alkyl group. Examples of the C_{10-22} alkyl group include dodecyl group, tetradecyl group, hexadecyl group, octadecyl group, oleyl group, and hydrocarbon group derived from oligomer of olefin such as propylene and butylene. Examples of the C_{3-10} alkyl group include propyl group, butyl group, hexyl group, octyl group, and nonyl group.

The phenate to be used in the present invention is a phenolate. Preferred examples of such a phenolate include salts of sulfide of an alkylphenol having a C_{8-30} alkyl group added thereto with alkaline earth metals (preferably calcium, magnesium, barium). These phenolates are described, for example, in JP-A-57-142393. As one of these phenolates there is commercially available COSMO PAD210 from Cosmo Oil Co., Ltd.

The salicylate to be used in the present invention is preferably a salicylate of an alkaline earth metal. Typical examples of such a salicylate of an alkaline earth metal include salicylates of calcium and magnesium. In general, these salicylates can be obtained by alkylating phenol with a C_{14-18} α-olefin, making a salt of the alkylated phenol with an alkaline metal, allowing the salt to undergo Kolbe-Schmitt reaction to introduce carboxyl groups thereinto, and then subjecting the material to double decomposition or the like to produce a salicylate of an alkaline earth metal. These salicylates are described, for example, in JP-B-61-24560 and JP-B-61-24561.

The component (B) is preferably blended in the composition of the present invention in an amount of 0.01 to 10 wt%, particularly 0.1 to 5 wt%. If the content of the component (B) falls below 0.01 wt%, a sufficient effect of inhibiting the viscosity decreases cannot be attained. On the contrary, if the content of the component (B) exceeds 10 wt%, the improvement in such an effect cannot be expected too much.

With the addition of only the components (A) and (B), the composition of the present invention can be rendered insusceptible to viscosity decreases. Further, with the addition of one or more selected from the group consisting of sulfur compounds, phosphorus compounds and chlorine compounds represented by the following general formulae (I) to (XI), the composition of the present invention can be rendered insusceptible also to viscosity increases or gelation.

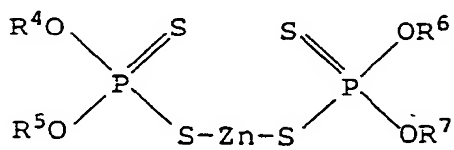
(I) Hydrocarbon sulfide represented by the general formula (2):

$$R^2\text{-}S_x\text{-}(R^3\text{-}S_x)_n\text{-}R^2 \qquad (2)$$

wherein R^2 represents a hydrocarbon group; R^3 represents a divalent hydrocarbon group; the suffix x represents an integer 1 or more and may be the same or different in the recurring unit; and the suffix n represents 0 or an integer 1 or more.

(II) Sulfurized oil or fat which is the reaction product of an oil or fat and sulfur.

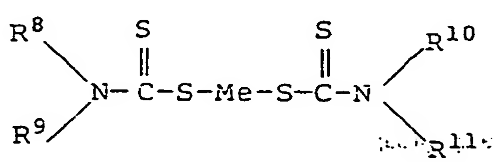
(III) Zinc dithiophosphate represented by the general formula (3):



(3)

wherein R^4, R^5, R^6 and R^7 which may be the same or different each represents a hydrocarbon group.

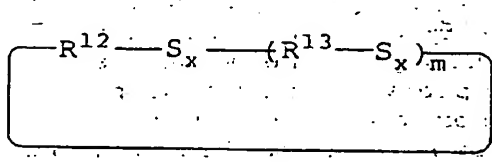
(IV) Dialkyldithiocarbamic acid metal salt represented by the general formula (4):



(4)

wherein R^8, R^9, R^{10} and R^{11} which may be the same or different each represents an alkyl group; and Me represents a metal selected from the group consisting of Zn, Pb, Mo and Sb.

(V) Elemental sulfur.
(VI) Hydrocarbon sulfide represented by the general formula (5):

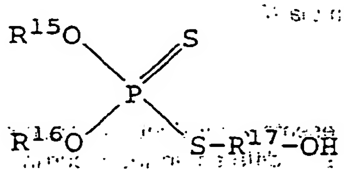


(5)

wherein R^{12} and R^{13} each represents a divalent hydrocarbon group; the suffix x represents an integer 1 or more and may be the same or different in the recurring unit; and the suffix m represents 0 or an integer 1 or more.
(VII) Phosphoric ester, phosphorous ester, thiophosphoric ester or dithiophosphoric ester represented by the general formula (6):

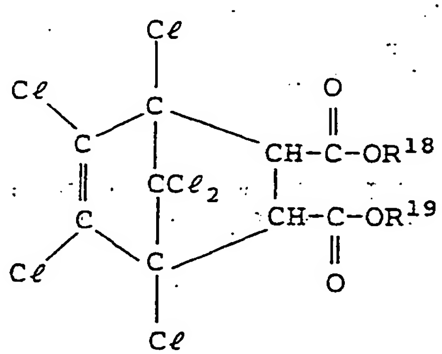
$(R^{14})_bH_{3-b}X_3PX_c$ (6)

wherein R^{14} represents a monovalent hydrocarbon; the suffix b represents an integer 1, 2 or 3; the suffix c represents 0 or an integer 1; and X represents an oxygen atom or sulfur atom.
(VIII) Alkylamine salt of acidic phosphoric ester, acidic phosphorous ester, acidic thiophosphoric ester or acidic dithiophosphoric ester represented by the general formula (6).
(IX) Reaction product of hydrocarbon and phosphorus sulfide.
(X) Composition containing phosphorus and nitrogen obtained by neutralizing with an amine the reaction product of (i) a hydroxyl-substituted triester of dithiophosphoric acid represented by the general formula (7):



(7)

(wherein R^{15} and R^{16} each represents a monovalent hydrocarbon; and R^{17} represents a divalent hydrocarbon) and (ii) a phosphoric acid, phosphorus oxide or halogenated phosphorus.
(XI) Diester represented by the general formula (8):



(8)

wherein R^{18} and R^{19} each represents an alkyl group.

These sulfur compounds, phosphorus compounds and chlorine compounds will be further described hereinafter.

In the sulfur compound (I) repres nted by the general formula (2), the group R^2 is a hydrocarbon. Examples of such a hydrocarbon group include C_{2-20} straight-chained or branched, saturated or unsatu-

rated aliphatic hydrocarbon group (e.g., alkyl, alkenyl), and C_{6-26} aromatic hydrocarbon group. Specific examples of these hydrocarbon groups include ethyl group, propyl group, butyl group, nonyl group, dodecyl group, propenyl group, butenyl group, benzyl group, phenyl group, tolyl group, and hexylphenyl group. The group R^3 is a divalent hydrocarbon group such as C_{2-20} straight-chained or branched aliphatic hydrocarbon group and C_{6-26} aromatic hydrocarbon group. Specific examples of these divalent hydrocarbon groups include ethylene group, propylene group, butylene group, and phenylene group. Typical examples of the sulfur compound (I) include olefin sulfide, and polysulfide compound represented by the general formula R^2-S_x-R^2 (in which x is an integer 2 or more). Specific examples of the sulfur compound (I) include diisobutyl disulfide, dioctyl polysulfide, ditertiary nonyl polysulfide, ditertiary butyl polysulfide, dibenzyl polysulfide, sulfurized olefins prepared by sulfurizing olefins such as polyisobutylene and terpenes with a sulfurizing agent such as sulfur, and the reaction product of isobutylene and sulfur, which is presumed, but not proven, to have the general formula:

$$CH_2=C(CH_3)-CH_2-S_x-\left(CH_2-C(CH_3)_2-S_x\right)_n-CH_2-C(CH_3)=CH_2$$

and/or the general formula:

$$CH_2=C(CH_3)-CH_2-S_x-CH_2-C(CH_3)_2-S_x-CH_2-C(CH_3)=CH_2$$

wherein X and n have the same meanings as described above.

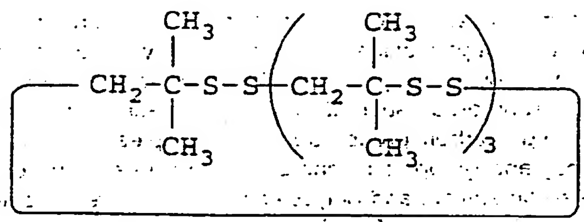
The component (II) is a hardened oil or fat that is the reaction product of an oil or fat with sulfur. Illustrative fats and oils include lard, tallow, whale oil, palm oil, coconut oil, rapeseed oil and many other animal and vegetable oil and fats. The reaction products of these fats and oils and sulfur are not simple in their chemical structure and instead are mixtures of various chemical structures which themselves are not clearly identified.

In the zinc dithiophosphate (III), R^4, R^5, R^6 and R^7 which may be the same or different each represents a hydrocarbon group such as C_{3-20}, particularly C_{3-12} straight-chained or branched, saturated or unsaturated aliphatic hydrocarbon group (e.g., alkyl, alkenyl) and C_{6-20} aromatic hydrocarbon group. Specific examples of these hydrocarbon groups include propyl group, butyl group, nonyl group, dodecyl group, octenyl group, phenyl group, and tolyl group. Specific examples of the zinc dithiophosphate (III) include zinc diisobutyldithiophosphate, zinc dipentyldithiophosphate, zinc di-1-methylheptyldithiophosphate, zinc di-2-ethylhexyldithiophosphate, and zinc diphenyldithiophosphate.

In the dialkyldithiocarbamate (IV), R^8, R^9, R^{10} and R^{11} which may be the same or different each represents an alkyl group preferably having 3 to 20 carbon atoms, particularly 3 to 12 carbon atoms, such as propyl group, butyl group, nonyl group and dodecyl group. In the compound (IV), Me represents a metal selected from the group consisting of Zn, Pb, Mo and Sb. Specific examples of the compound (IV) include zinc diisobutyldithiocarbamate, zinc diamyldithiocarbamate and zinc didodecyldicarbamate.

Sulfur as the component (V) is used in powder form. When it is put into the polyorganosiloxane fluid and heated to about 150 to 250°C with stirring, it will be dissolved or uniformly dispersed in the polyorganosiloxane fluid.

In the cyclic sulfur compound (VI), R^{12} and R^{13} each represents a divalent hydrocarbon group such as C_{2-20} straight-chained or branched aliphatic hydrocarbon group and C_{6-26} aromatic hydrocarbon group. Specific examples of these divalent hydrocarbon groups include ethylene group, propylene group, butylen group, and phenyl ne group. An example of the sulfur compound (VI) is a compound represented by the following general formula:



The foregoing cyclic sulfur compound may be prepared by the synthesis method described, for example, in U.S. Patent 3,925,414. For example, an olefin such as isobutylene may be reacted with sulfur monohalide to give a product which is then reacted with an alkali mercaptide.

In the phosphorus additive represented by the general formula (6), the group R^{14} is a monovalent hydrocarbon group such as C_{5-20} straight-chained or branched, saturated or unsaturated aliphatic hydrocarbon group (e.g., alkyl, alkenyl), C_{6-26} aromatic hydrocarbon group and cycloalhyl group. Specific examples of these phosphorus additives include monooctyl phosphate, dioctyl phosphate, trioctyl phosphate, dioctyl phosphite, trioctyl phosphite, dioctyl thiophosphate, trioctyl thiophosphate, didecyl phosphate, didecyl phosphite, didodecyl phosphate, tridodecyl phosphate, didodecyl phosphite, tridodecyl phosphite, tridodecyl thiophosphate, trihexadecyl phosphate, trihexadecyl phosphite, trihexadecyl thiophosphate, trioctadecenyl phosphate, trioctadecenyl phosphite, trioctadecenyl thiophosphate, tri(octylphenyl) phosphate, tri(octylphenyl) phosphite, tri(octylphenyl) thiophosphate, tri(octylcyclohexyl) phosphate, and tridecyl dithiophosphate.

The component (VIII) is an alkylamine salt of acidic phosphoric ester, acidic phosphorous ester, acidic thiophosphoric ester or acidic dithiophosphoric ester represented by the general formula (6). Among the foregoing components, the acidic phosphoric ester is particularly suitable for use in a viscous coupling. Specific examples of these compounds include butyl acid phosphate, 2-ethylhexyl acid phosphate, octyl acid phosphate, lauryl acid phosphate, oleyl acid phosphate, and tolyl acid phosphate. The alkylamine to be used for the neutralization of these compounds is represented by the general formula of $NR^{23}R^{24}R^{25}$ (R^{23}, R^{24} and R^{25} each represents a monovalent hydrocarbon group or hydrogen atom, with the proviso that at least one of R^{23}, R^{24} and R^{25} is a hydrocarbon group). Specific examples of these compounds include dibutylamine, octylamine, dioctylamine, laurylamine, dilaurylamine, coconut amine, and tallow amine. Examples of these compounds which are commercially available in the form of salts include "Ortholeum 535" (Du Pont), "Vanlube 672" (Vanderbuild), and "Irgalube 349" (Ciba Geigy).

The hydrocarbon as a starting material of the component (IX) is a hydrocarbon having one or more double bonds and containing about 5 to 20 carbon atoms. Examples of phosphorus sulfide as the other starting material include P_2S_5, P_2S_4, and P_2S_3. Examples of the reaction product of such a hydrocarbon and phosphorus sulfide include those obtained by phosphosulfurizing terpenes, low molecular polybutylenes or olefins.

In the general formula (7) as a starting material of the reaction product (X), R^{15} and R^{16} may be the same or different and each represents a monovalent hydrocarbon group such as C_{1-25} straight-chained or branched, saturated or unsaturated aliphatic hydrocarbon group (e.g., alkyl, alkenyl), C_{6-26} aromatic hydrocarbon group and cycloalkyl group. Preferably, R^{15} and R^{16} are the same and each represents an alkyl group. R^{17} represents a divalent hydrocarbon group having less than about 20 carbon atoms, such as alkylene group and aryl-substituted alkylene group. The amine to be used for the neutralization of the reaction produce (X) is an aliphatic, aromatic or alicyclic primary amine having about 5 to 20 carbon atoms.

Specific examples of the foregoing compound containing phosphorus and nitrogen include a compound obtained by neutralizing the reaction product of ester hydroxyethyl-O,O'-dihexyldithiophosphate and phosphorus pentaoxide with dodecylamine, a compound obtained by neutralizing the reaction product of ester hydroxypropyl-O,O'-dihexyldithiophosphate and phosphorus pentaoxide with octadecylamine, a compound obtained by neutralizing the reaction product of ester hydroxyhexyl-O,O'-dihexyldithiophosphate and phosphorus pentaoxide with dodecylamine, a compound obtained by neutralizing the reaction product of ester phenylhydroxyethyl-O,O'-dihexyldithiophosphate and phosphorus pentaoxide with dodecylamine, and a compound obtained by neutralizing the reaction product of ester hydroxypropyl-O,O'-dihexyldithiophosphate and phosphorus pentaoxide with octadecylamine. The foregoing compound containing phosphorus and nitrogen can be normally prepared by reacting 1 mol of an inorganic phosphorus chemical with about 1 to 5 mols of triester dithiophosphate to produce an acidic int rmediate, and then substantially neutralizing the intermediate with an amine. If the foregoing hydrocarbon sulfide has too low a molecular weight, it is subject

to evaporation loss. On the contrary, if the hydrocarbon sulfide has too high a molecular weight, it cannot thoroughly exert its desirable effect. On the other hand, if the phosphorus-containing organic compound has too few carbon atoms, it cannot thoroughly exert its desirable effect. The phosphorus-containing organic compound having too many carbon atoms are hardly available.

In the component (XI) represented by the general formula (8), R^{18} and R^{19} which may be the same or different is preferably a C_{4-8} alkyl group. Preferably, R^{18} and R^{19} are the same and each represents an alkyl group. Specific examples of diester include dibutyl chlorendate, dihexyl chlorendate, dioctyl chlorendate, and di-2-ethylhexyl chlorendate.

The foregoing diester can be prepared by reacting the carboxyl group in chlorendic acid with a C_{4-8} alcohol. In another nomenciature, chlorendic acid is represented as 1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-hepto-5-ene-2,3-dicarboxylic acid. It can be prepared by a so-called Diels-Alder addition of the corresponding chlorinated cyclopentadiene and maleic anhydride.

The sulfur compound (I) is preferably blended in the fluid composition for use in a viscous coupling according to the present invention in an amount of about 0.01 to 10% by weight (hereinafter simply referred to as "%"), particularly about 0.1 to 5%.

If the content of the component (I) is too low, the desired effect cannot be thoroughly attained. On the contrary, if the content of the component (I) is too high, the component (A) or (I) will undergo thermal deterioration to an undesirably extent. This is also the case for the components (II) to (XI). A particularly preferred content of elemental sulfur as component (V) ranges from about 0.01 to 5.0%, more preferably from about 0.05 to 2.0%. With the composition of the present invention, the component (B) that is to be mixed with the component (A) preferably is dissolved in the polyorganosiloxane serving as the base oil. However, this is not necessarily the essential requirement and the component to be added may be merely dispersed in the highly viscous base oil. If desired, the component to be added may react with the base oil.

The components (I) to (XI) exhibit their intended effects even if they are added individually to the polyorganosiloxane represented by (A). Needless to say, two or more, or two to six, of these components may be added in admixture to the polyorganosiloxane. In the latter case, the total content of the additional components (I) to (XI) is preferably within the range of from about 0.01 to 10%. Unless otherwise specified, the contents of the components to be incorporated in the composition of the present invention are expressed on the basis of the total amount of the composition.

It should be noted that the composition of the present invention may comprise conventional heat stabilizers or other common additives incorporated therein. Taking into account the fact that the composition of the present invention is to be exposed to various hostile conditions of its service as a working fluid in viscous couplings, it will be desirable in certain instances to additionally incorporate conventional heat stabilizers to the composition. Examples of such additives include phosphorus compounds and chlorine compounds as disclosed in JP-A-2-91196, known oxidation inhibitors, corrosion inhibitors, and metal deactivators.

While the composition of the present invention is useful as a fluid composition for use in a viscous coupling, it is also suitable as a fluid coupling such as fan coupling.

The fluid composition of the present invention for use in a viscous coupling is insusceptible to viscosity decreases due thermal decomposition and viscosity increases or gelation and thus remains stable during a prolonged use. The working fluid of the present invention also offers the additional advantage of improving the wear resistance of the plate assemblies in the viscous coupling, thereby enhancing its durability as well as the reliability of an automobile using that viscous coupling.

The present invention will be further described in the following examples, but the present invention should not be construed as being limited thereto. The viscosity values as defined hereinafter were determined at 25°C unless otherwise specified.

EXAMPLES 1 TO 11

Fluid compositions having the following formulations were prepared by an ordinary method. These specimens were then subjected to the following tests. The results are set forth in Table 3.

All the compositions excepting those prepared in Comparative Example 1 were prepared by mixing at 60°C for 1 hour with stirring the necessary components in the proportions indicated in Tables 1 and 2. All of the polyorganosiloxane reagents used in Examples 1 to 11 and Comparativ Example 1 to 3 had the terminal ends of their molecular chain terminated with a trimethylsilyl group. The calcium sulfonate used in Examples 1 to 11 had a specific gravity (15/4°C) of 1.125 and a calcium proportion of 12.0% by weight (Lubrisol 74 available from Nippon Lubrisol K.K.). The calcium salicylate used in Examples 1 to 11 had a specific gravity (15/4°C) of 1.025 and a calcium proportion of 6.0% by weight (Shell AC60C available from

Shell Kagaku K.K.). The calcium phenate used in Examples 1 to 11 had a specific gravity (15/4 °C) of 1.01 and a calcium proportion of 5.2% by weight (Oloa 218A available from Olonite Japan K.K.).

The ditertiary nonyl polysulfide used in Examples 2 and 10 and Comparative Example 3 was "TNPS" (trade name of Nippon Thiochemical Co., Ltd.) having a specific gravity (15 °C/4 °C) of 1.045 and a sulfur content of 37.5% by weight. Sulfurized olefin used in Examples 3, 6 and 11 and Comparative Example 2 was "HITEC 053" (trade name of Nippon Cooper Co., Ltd.) having a specific gravity (15 °C/4 °C) of 1.14, a sulfur content of 46.5% by weight and a viscosity of 9.0 centistokes at 100 °C.

The tricresyl phosphate used in Examples 4 and 8 and Comparative Example 3 was a product of Daihachi Kagaku K.K. having a specific gravity (15 °C/4 °C) of 1.17, a phosphorus content of 8.4% by weight and a total acid number of 0.05 mg KOH/g. The zinc dialkyldithiophosphate (1) used in Example 5 contained an alkyl group having 6 carbon atoms and was "HITEC 653" (trade name of Nippon Cooper Co., Ltd.) having a specific gravity (15 °C/4 °C) of 1.10, a zinc content of 8.5% by weight and a sulfur content of 17.0% by weight.

The siloxane having an aromatic group used in Example 11 had a specific gravity (25 °C) of 1.080 and a viscosity of 115 centistokes. Ethyl 702 used was "HITIC 4710" (trade name of Ethyl Co., Ltd.). The metal deactivator used was "AMOCO 8087" (trade name of Amoco Co., Ltd.).

TABLE 1

Example No.	Composition	wt%
1	Polydimethylsiloxane (300,000 cSt)	99.8
	Calcium sulfonate	0.2
2	Polydimethylsiloxane (300,000 cSt)	99.2
	Ditertiary nonyl polysulfide	0.5
	Calcium sulfonate	0.3
3	Polydimethylsiloxane (300,000 cSt)	99.2
	Olefin sulfide	0.5
	Calcium sulfonate	0.3
4	Polydimethylsiloxane (300,000 cSt)	98.7
	Tricresyl phosphate	1.0
	Calcium sulfonate	0.3

TABLE 1 (cont'd)

Example No.	Composition	wt%
5	Polydimethylsiloxane (300,000 cSt)	98.5
	Zinc dialkyldithiophosphate	1.0
	Calcium sulfonate	0.5
6	Polydimethylsiloxane (300,000 cSt)	98.5
	Olefin sulfide	1.0
	Calcium salicylate	0.5
7	Polydimethylsiloxane (300,000 cSt)	99.7
	Calcium salicylate	0.3
8	Polydimethylsiloxane (300,000 cSt)	98.5
	Tricresyl phosphate	1.0
	Calcium salicylate	0.5
9	Polydimethylsiloxane (300,000 cSt)	99.5
	Calcium phenate	0.5
10	Polydimethylsiloxane (300,000 cSt)	98.5
	Ditertiary nonyl polysulfide	1.0
	Calcium phenate	0.5
11	Polydimethylsiloxane (300,000 cSt)	98.4
	Olefin sulfide	0.5
	Calcium sulfonate	0.3
	Siloxane containing aromatic group	0.5
	Ethyl 702	0.2
	Metal deactivator	0.1

TABLE 2

Comparative Example No.	Composition	wt%
1	Polydimethylsiloxane (300,000 cSt)	100.0
2	Polydimethylsiloxane (300,000 cSt) Olefin sulfide	99.5 0.5
3	Polydimethylsiloxane (300,000 cSt) Ditertiary nonyl polysulfide Tricresyl phosphate	99.0 0.5 0.5

The compositions prepared in the foregoing examples and comparative examples were evaluated for their performance as working fluids for use in a viscous coupling. The results are set forth in Tables 3 and 4.

For the evaluation of thermal stability, about 40 g of the specimen oil was measured out in a 50-cc beaker (inner diameter: 3 cm). The beaker was horizontally placed in a rotary air circulation constant temperature bath where it was then heated to a temperature of 180°C for 120 hours to determine the viscosity change.

For the evaluation of applicability to machine, a viscous coupling having a set of 31 plates was charged with the compositions to a fill ratio of 82 vol%. The viscous coupling was then continuously rotated at a differential velocity of 20 r.p.m. for 400 hours with the fluid temperature kept at 135°C. The resulting changes in torque and viscosity were determined.

TABLE 3

Results of thermal stability test	
Example No.	Viscosity change (%)
1	-1
2	-3
3	-3
4	-2
5	-3
6	-4
7	-1
8	-2
9	-1
10	-3
11	-3
Comparative Example 1	-10
Comparative Example 2	-51
Comparative Example 3	-52

TABLE 4

Results of applicability test		
Example No.	Torque change (%)	Viscosity change (%)
3	-13	-18
6	-13	-20
10	-15	-25
Comparative Example 2	-21	-38

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A fluid composition for use in a viscous coupling, comprising the following components (A) and (B):
   (A) A polyorganosiloxane having a viscosity of 500 to 500,000 centistokes at 25 °C represented by the following average unit formula (1):

$$(R^1)_a SiO_{\frac{4-a}{2}}$$

   wherein R^1 represents a hydrocarbon group or halogenated hydrocarbon group; and the suffix $\underline{a}$ represents a number of 1.9 to 2.1; and
   (B) one or more selected from the group consisting of sulfonate, phenate and salicylate.

2. The fluid composition for use in a viscous coupling according to Claim 1, wherein the content of said component (A) is from 90 to 99.99 wt% and the content of said component (B) is from 0.01 to 10 wt%.

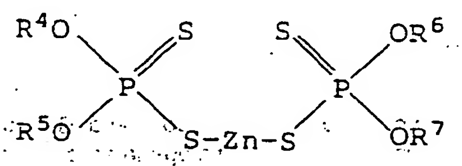
3. The fluid composition for use in a viscous coupling according to Claim 1, wherein the viscosity of said component (A) at 25 °C is from 3,000 to 400,000 cSt.

4. The fluid composition for use in a viscous coupling according to Claim 1, wherein the viscosity of said component (A) at 25 °C is from 5,000 to 400,000 cSt.

5. The fluid composition for use in a viscous coupling according to Claim 1, which comprises one or more selected from the group consisting of sulfur, sulfur compounds, phosphorus compounds and chlorine compounds represented by the following general formulae (I) to (XI):
   (I) Hydrocarbon sulfide represented by the general formula (2):

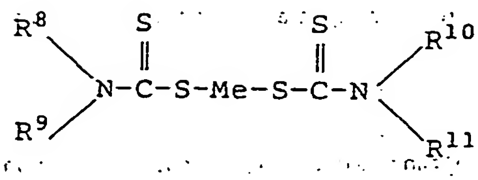
$$R^2\text{-}S_x\text{-}(R^3\text{-}S_x)_n\text{-}R^2 \quad (2)$$

   wherein R^2 represents a hydrocarbon group; R^3 represents a divalent hydrocarbon group; the suffix $\underline{x}$ represents an integer 1 or more and may be the same or different in the recurring unit; and the suffix $\underline{n}$ represents 0 or an integer 1 or more;
   (II) Sulfurized oil or fat which is the reaction product of an oil or fat and sulfur;
   (III) Zinc dithiophosphate represented by the general formula (3):



(3)

   wherein R^4, R^5, R^6 and R^7 which may be the same or different each represents a hydrocarbon group;
   (IV) Dialkyldithiocarbamic acid metal salt represented by the general formula (4):



(4)

wherein R^8, R^9, R^{10} and R^{11} which may be the same or different each represents an alkyl group; and Me represents a metal selected from the group consisting of Zn, Pb, Mo and Sb;

(V) Elemental sulfur;

(VI) Hydrocarbon sulfide represented by the general formula (5):

$$\boxed{-R^{12}-S_x-(R^{13}-S_x)_m-} \qquad (5)$$

wherein R^{12} and R^{13} each represents a divalent hydrocarbon group; the suffix x represents an integer 1 or more and may be the same or different in the recurring unit; and the suffix m represents 0 or an integer 1 or more;

(VII) Phosphoric ester, phosphorous ester, thiophosphoric ester or dithiophosphoric ester represented by the general formula (6):

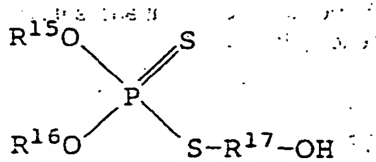
$(R^{14})_bH_{3-b}X_3PX_c$ (6)

wherein R^{14} represents a monovalent hydrocarbon; the suffix b represents an integer 1, 2 or 3; the suffix c represents 0 or an integer 1; and X represents an oxygen atom or sulfur atom;

(VIII) Alkylamine salt of acidic phosphoric ester, acidic phosphorous ester, acidic thiophosphoric ester or acidic dithiophosphoric ester represented by the general formula (6);

(IX) Reaction product of hydrocarbon and phosphorus sulfide;

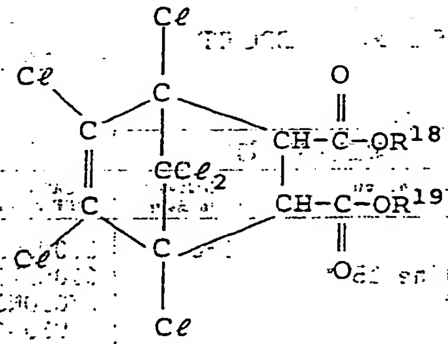
(X) Composition containing phosphorus and nitrogen obtained by neutralizing with an amine the reaction product of (i) a hydroxyl-substituted triester of dithiophosphoric acid represented by the general formula (7):



(7)

(wherein R^{15} and R^{16} each represents a monovalent hydrocarbon; and R^{17} represents a divalent hydrocarbon) and (ii) a phosphoric acid, phosphorus oxide or halogenated phosphorus; and

(XI) Diester represented by the general formula (8):



(8)

wherein R^{18} and R^{19} each represents an alkyl group.

6. The fluid composition for use in a viscous coupling according to Claim 5, wherein the added amount of said components (I) to (XI) was from 0.01 to 10 wt%.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 8776

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y	GB-A-2 206 887 (COSMO OIL) * page 4, line 22 - page 6, line 15 * * page 15, line 9 - line 18 *	1-6	C10M169/04 C10M171/00 //C10N30/08, C10N40/00, (C10M169/04, 107:50,129:10, 129:54,125:06, 131:12,135:04, 135:06,135:10, 135:18,135:22, 137:02,137:04, 137:08,137:10, 159:12)
Y	EP-A-0 393 732 (KING INDUSTRIES) * claims 1,20 * * column 7, line 46 - column 8, line 20 *	1-6	
A	FR-A-2 539 426 (IDEMITSU KOSAN COMPANY LIMITED) * page 5, line 10 - line 11 * * page 7; examples 2,6 *	1	
A	EP-A-0 397 507 (TONEN CORPORATION) * claim 1 * * page 3, line 3 - line 27 * * page 5, line 51 - page 6, line 17 *	5,6	
A	GB-A-1 309 032 (DOW CORNING CORPORATION) * page 1, line 49 - line 71 *	5,6	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
D,A	DATABASE WPI Week 9019, Derwent Publications Ltd., London, GB; AN 90-144410[19] & JP-A-2 091 196 (COSMO SEKIYU) 30 March 1990 * abstract *	5,6	C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 February 1994	Hilgenga, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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